INTERNATIONAL STANDARD

ISO 8332

Second edition
1997-04-01

Rubber compounding ingredients — Sulfur — Methods of test

Ingrédients de mélange du caoutchouc — Soufre — Méthodes d'essai

Reference number
ISO 8332:1997(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 8332 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry.*

This second edition cancels and replaces the first edition (ISO 8332:1993), in which the methods for the determination of the thermal reversion of insoluble sulfur have been revised (for details, see subclause 8.1 of this edition).

Annexes A and B of this International Standard are for information only.

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Introduction

There are two main types of sulfur, viz:

a) rhombic sulfur;

b) insoluble sulfur (sometimes referred to as amorphous sulfur).

Both types of sulfur can be used as a rubber compounding ingredient either in their natural form or with oil added. Sulfur may also be coated with, for example, magnesium carbonate or silica. These additives act as an aid to dispersion in the rubber compound. Sulfur is available in varying degrees of fineness. Insoluble sulfur may also contain an amount of rhombic sulfur, as insoluble sulfur tends to revert back to the rhombic state on storage.

These considerations are each the subject of the methods of test specified in this International Standard.

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Rubber compounding ingredients — Sulfur — Methods of test

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. The standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies methods of test for determining the main physical and chemical properties of sulfur used for compounding dry rubber.

NOTE — The typical levels for the relevant properties of sulfur for use as a rubber compounding ingredient are contained in annex A. This annex is not an integral part of the Standard, however.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 565:1990, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings.*

ISO 842:1984, *Raw materials for paints and varnishes — Sampling.*

ISO 2590:1973, *General method for the determination of arsenic — Silver diethyldithiocarbamate photometric method.*

ISO 3425:1975, *Sulphur for industrial use — Determination of ash at 850-900 °C and of residue at 200 °C.*

ISO 3426:1975, *Sulphur for industrial use — Determination of loss in mass at 80 °C.*

ISO 3704:1976, *Sulphur for industrial use — Determination of acidity — Titrimetric method.*

ISO 3705:1976, *Sulphur for industrial use — Determination of arsenic content — Silver diethyldithiocarbamate photometric method.*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

ISO/TR 9272:1986, *Rubber and rubber products — Determination of precision for test method standards.*

3 Physical and chemical properties

After sampling with a stainless-steel sampling tool in accordance with ISO 842, the physical and chemical properties of sulfur used as a rubber compounding ingredient shall be determined by the following test methods:

Property	Test method	
Total sulfur [% (*m*/*m*)]	Clause 4	of this International Standard
Fineness (sieve residue)	Clause 5	of this International Standard
Oil content [% (*m*/*m*)]	Clause 6	of this International Standard
Insoluble sulfur [% (*m*/*m*)]	Clause 7	of this International Standard
Thermal reversion (%)	Clause 8	of this International Standard
Acidity [as H_2SO_4, % (*m*/*m*)]	ISO 3704	
Loss in mass at 80 °C [% (*m*/*m*)]	ISO 3426	
Ash [% (*m*/*m*)]	ISO 3425	
Arsenic [% (*m*/*m*)]	ISO 3705, ISO 2590	

4 Determination of total sulfur content

4.1 Principle

The sulfur in a test portion is first converted to thiosulfate which is then determined by titration with an iodine solution.

4.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.2.1 Sodium sulfite solution, 50 g/dm^3. Dissolve 50 g of sodium sulfite in 1 dm^3 of water.

4.2.2 Standard volumetric iodine solution, $c(I_2)$ = 0,05 mol/dm^3, freshly prepared and standardized.

4.2.3 Formaldehyde solution, 40 % (*V*/*V*).

4.2.4 Glacial acetic acid.

4.2.5 Wetting-out solution, consisting of a 20 g/dm^3 solution of an alkylaryl sulfonate (e.g. sodium dodecylbenzene sulfonate) in water.

4.2.6 Soluble-starch solution, freshly prepared.

4.3 Procedure

4.3.1 Weigh, to the nearest 0,1 mg, 0,2 g of the sulfur sample (m_0) on a tared watch glass. Using a Pasteur pipette, add approximately 1 cm^3 of wetting solution (4.2.5). Transfer the mixture to a 250 cm^3 flask via a small glass funnel using a stream of the sodium sulfite solution (4.2.1) from a 50 cm^3 measuring cylinder. Add a few antibumping granules, fix an air condenser in position and place the whole on an electrically heated sand-bath.

Adjust the sand-bath temperature control so that the contents of the flask simmer gently. It is most important to ensure that frothing or the formation of large bubbles is avoided, otherwise particles of sulfur can migrate up the walls of the flask and into the condenser, where they no longer react.

4.3.2 After 2 h, the sulfur will have dissolved. [The time to achieve complete dissolution is dependent on the size of the sample particles. To ensure a reaction time of 2 h, it is necessary either to pre-grind the sample to pass through a 125 µm screen (see ISO 565) or to know in advance that the sample meets this requirement.]

Remove the flask and cool it to 15 °C. Wash the walls of the condenser with water and collect the washings in the flask. Remove the condenser. Transfer the contents of the flask into a 100 cm^3 graduated flask. Wash out the sample flask with water and add the washings to the graduated flask. Make up to the 100 cm^3 mark with water. Stopper and shake to make homogenous.

4.3.3 Pipette 25 cm^3 of the test solution thus prepared into a 250 cm^3 conical flask. Measure out and add 10 cm^3 of the formaldehyde solution (4.2.3), 25 cm^3 of acetic acid (4.2.4) and 1 cm^3 of the starch solution (4.2.6). Cool to 15 °C, then titrate with the iodine solution (4.2.2) from a burette until a blue colour is obtained which persists for 15 s. Repeat the titration with two further 25 cm^3 portions of the test solution and average the results for the calculation.

4.3.4 Carry out a blank determination omitting the test portion.

4.4 Expression of results

Calculate the total sulfur content, expressed as a percentage by mass, from the formula

$$\frac{(V_1 - V_0)\, c \times 4 \times 6{,}4}{m_0}$$

where

V_0 is the volume, in cubic centimetres, of iodine solution (4.2.2) used to titrate the blank (see 4.3.4);

V_1 is the volume, in cubic centimetres, of iodine solution (4.2.2) used to titrate the test portion (see 4.3.3);

c is the exact concentration, in moles of I_2 per cubic decimetre, of the iodine solution (4.2.2);

m_0 is the mass, in grams, of the test portion (see 4.3.1).

4.5 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

b) all details necessary for the identification of the sample;

c) the total sulfur content;

d) the date of the test;

e) details of any deviation from the standard test procedure.

5 Determination of sieve residue

5.1 Principle

A test portion is passed through sieves of specified mesh opening and the residue retained is weighed.

Two procedures are specified, viz:

a) a wet procedure for all oil-treated grades of sulfur;

b) a dry procedure for all other (i.e. non-oil-treated) grades.

In the case of extremely fine grade sulfurs, the wet procedure shall be used.

5.2 Wet procedure

5.2.1 Apparatus

5.2.1.1 Metal funnel (A), about 200 mm in diameter, terminating at the foot in a short cylindrical outlet (see figure 1) in which is inserted a shallow removable cup (B), on the bottom of which a wire-cloth sieve (C) (5.2.1.2) is soldered; this is 25 mm in diameter. Water under pressure is supplied by a tube (D) fitted with a nozzle designed to discharge a spreading jet through the sieve; the distance of the orifice from the sieve can be adjusted. The recommended minimum water pressure is 200 kPa (2 bar). The tube is provided with a filter (H) to remove any solid particles from the water; this filter shall be made from wire cloth at least as fine as the sieve (C), and shall be sufficiently large to prevent undue loss of pressure.

A similar arrangement is provided for another tube (E) used to supply a gentle stream of water for wetting the powder and keeping the volume of the liquid in the funnel constant during the test.

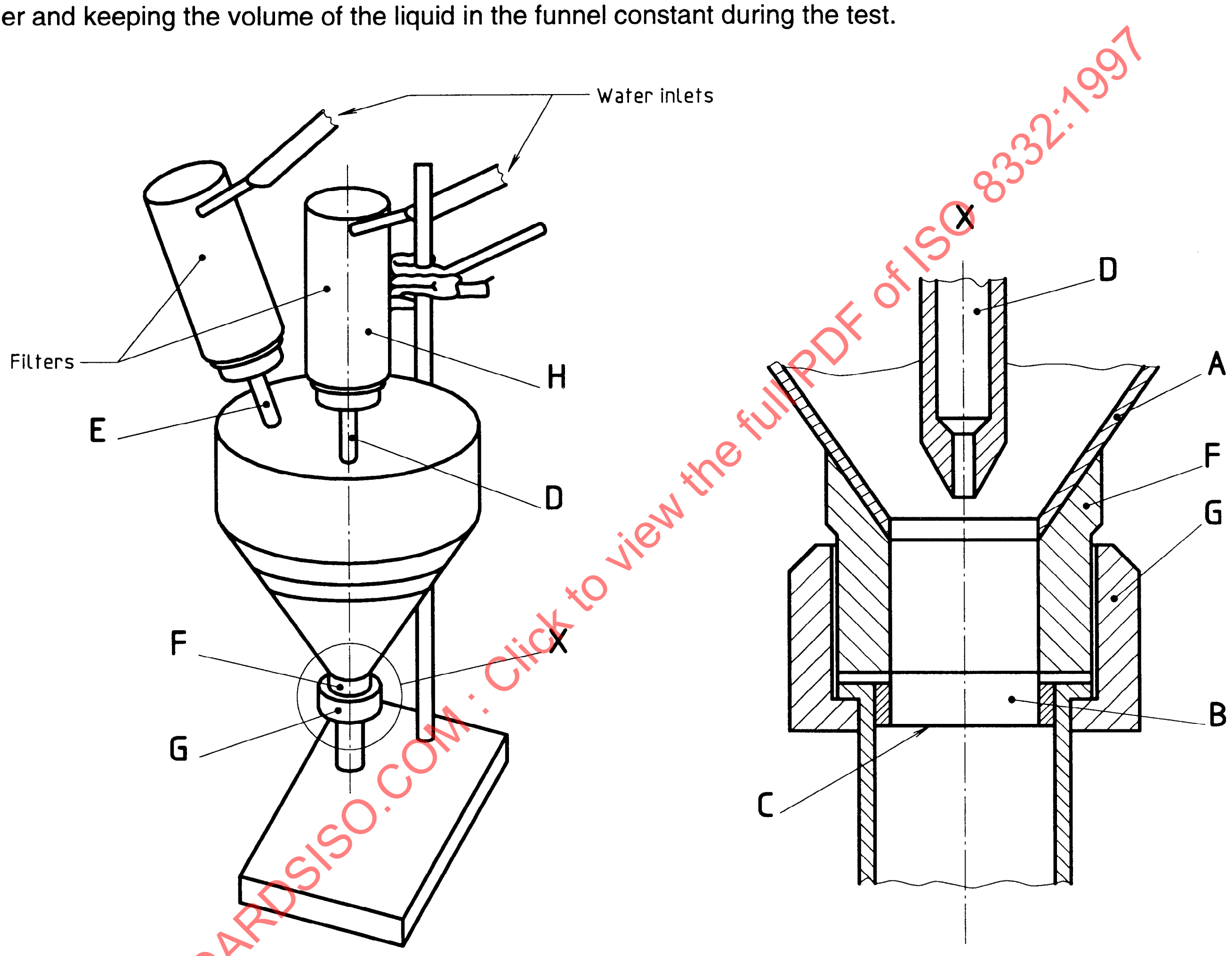

Figure 1 — Apparatus for determination of sieve residue (wet procedure)

5.2.1.2 Two sieves, of woven metal-wire cloth, having openings of nominal width 180 µm and 125 µm respectively, in accordance with ISO 565.

5.2.1.3 Flat brush, of camel hair, approximately 25 mm wide.

5.2.2 Determination

Mount a sieve cup with a sieve (5.2.1.2) of the required mesh, as agreed between the interested parties, in the apparatus. Allow water to flow through it for 3 min from tubes D and E. Examine the sieve for particles; if none are observed, the apparatus is ready for use. Dry the sieve cup at 105 °C ± 2 °C, weigh to 0,1 mg and mount in the apparatus, holding in place by union nut G. Weigh out about 25 g (m_0) of the sample accurately to 0,1 g, make into a slurry with 300 cm^3 of ethyl alcohol (industrial grade) in a beaker, and transfer quantitatively to the funnel (5.2.1.1).

NOTE 1 If the oil content of the sulfur is higher than 20 % (*m*/*m*), then a 20 g/dm^3 solution of alkylaryl sulfonate in water may be used instead of the ethyl alcohol.

About half fill the funnel with water from tube E. Slowly turn the high-pressure jet D on full and adjust the position of the nozzle under the liquid, in relation to the sieve, until there is little or no disturbance on the surface and the level is, if anything, sinking. Now use the supply from tube E to maintain the level constant, and wash down any solid matter adhering to the sides.

NOTE 2 When the best operating conditions have been so attained, the discharge pipe F below the sieve is completely filled with water; increasing the length of this column of liquid by adding a length of rubber tubing improves the efficiency of the apparatus.

Take a sample of the issuing water from time to time during the test and, when this is free from suspended matter, reduce the rate of flow from the jet. Wash down any residual material adhering to the sides of the funnel into the lower portion of the apparatus, and then adjust the jet to a rate which keeps the cylindrical portion full of violently agitated water. When the residual matter has been thoroughly washed in this way until the effluent runs clear (usually 3 or 4 minutes), turn off the jet and wash the grit down into the cup. Inspect the remaining sulfur and break up any loose agglomerates by brushing lightly with the camel-hair brush (5.2.1.3), subsequently washing them through the filter. Then wash the remaining grit into the cup.

Unscrew the milled union nut G, remove the discharge pipe and cup, and wash the contents of the latter with distilled water. Dry the cup and contents at 105 °C ± 2 °C and weigh to 0,1 mg. This mass, less the initial mass of the cup, equals the mass of the sieve residue (m_1).

5.2.3 Expression of results (wet procedure)

Calculate the sieve residue, expressed as a percentage by mass, using the formula

$$\frac{m_1 \times 100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of the residue on the sieve.

5.3 Dry procedure

5.3.1 Apparatus

5.3.1.1 Test-sieve assembly, of 200 mm diameter, having a fitting lid and receiver, with three sieves of aperture size 180 µm, 125 µm and 63 µm respectively, in accordance with ISO 565.

The sieves shall be of stainless-steel wire and shall fit together, one above the other, so that powder does not escape.

5.3.1.2 Mechanical sieve shaker, suitable for the sieve assembly (5.3.1.1), providing a gyrating and jolting action, preferably with an automatic timing device.

5.3.1.3 Analytical balance, accurate to 1 mg.

5.3.1.4 Flat brush, of camel hair, approximately 25 mm wide.

5.3.1.5 Three weighing bottles, two of capacity approximately 10 cm^3 and the third approximately 100 cm^3, with stoppers.

5.3.1.6 Sheets of glazed A4 paper.

5.3.1.7 Lightweight rubber-covered hammer.

5.3.2 Determination

Ensure that the three sieves (5.3.1.1) are free from any pervious residue by brushing with the camel-hair brush (5.3.1.4) and by blowing the sieves through with compressed air from above, with the sieve inverted, and tapping the sieve to dislodge any particles lodged in the mesh.

Fit the sieves one above the other with the largest-aperture sieve (180 µm) on top, then below it the sieve with the medium-size apertures (125 µm) and at the bottom the sieve with the smallest apertures (63 µm). Fit the receiver below the bottom sieve.

Blend the total sample, obtained in accordance with ISO 842 (using stainless-steel sampling tools), to ensure that finer and coarser particles are not segregated, then weigh out, to the nearest 1 mg, about 50 g of the representative sample, using the 100 cm^3 weighing bottle (5.3.1.5).

Pour the test portion thus obtained on to the top sieve and fit the lid. Reweigh the weighing bottle empty to obtain the mass of the test portion (m_0) by difference.

Install the sieve assembly in the mechanical shaker (5.3.1.2) (if available) and allow to shake for 5 min at a rate of 3 Hz (three shakes per second), then remove from the shaker. If no mechanical shaker is available, manually shake the stack for 5 min horizontally through an amplitude of 150 mm at a rate of 3 Hz, stopping after each minute to strike the base of the stack with the rubber-covered hammer (5.3.1.7) to help clear any blockages in the sieves.

Remove the lid and inspect the top sieve (180 µm). If material remains held on the top sieve, break up any loose agglomerates by brushing lightly with the camel-hair brush (5.3.1.4). Replace the lid, then lift the top sieve off the next sieve (125 µm) and similarly brush lightly any residue on this sieve. Then re-stack as before and shake mechanically or manually as before for a further 5 min.

Separate the stack of sieves completely and one at a time carefully transfer all the material held on each sieve to a clean, dry weighing bottle, previously weighted empty to 1 mg. (Use 10 cm^3 weighing bottles for the residues on the 180 µm and 125 µm sieves, and a 100 cm^3 weighing bottle for the residue on the 63 µm sieve.) To ensure complete transfer from sieve to weighing bottle, carefully pour the contents of each sieve on to a sheet of clean, glazed paper (5.3.1.6), then invert the sieve over the paper and tap lightly with the rubber-covered hammer to dislodge any jammed particles. Then remove the sieve and carefully lift the sheet of paper, form it into a chute and carefully pour the material on it into the weighing bottle, avoiding losses.

Finally, weigh each weighing bottle plus sieve residue to 1 mg and calculate the mass of the residue found on each sieve (m_1, m_2 and m_3).

5.3.3 Expression of results (dry procedure)

Calculate the residue on the 180 µm sieve, expressed as a percentage by mass, using the formula

$$\frac{m_1 \times 100}{m_0}$$

Calculate the total residue on both the 180 µm and 125 µm sieves, expressed as a percentage by mass, using the formula

$$\frac{\left(m_1 + m_2\right) \times 100}{m_0}$$

Calculate the total residue on all three sieves, expressed as a percentage by mass, using the formula

$$\frac{\left(m_1 + m_2 + m_3\right) \times 100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, found on the 180 µm sieve;

m_2 is the mass, in grams, found on the 125 µm sieve;

m_3 is the mass, in grams, found on the 63 µm sieve.

5.4 Test report

The test report shall include the following particulars:

a) a reference to this International Standard and the procedure used (wet or dry);

b) all details necessary for the identification of the sample;

c) wet method: the percentage residue retained on the sieve used; dry method: the cumulative totals for each sieve;

d) the date of the test;

e) details of any deviation from the standard test procedure.

6 Determination of oil content of oil-treated sulfur

6.1 Principle

Oil is extracted from the sample by using a solvent, and the solvent is then evaporated off and the mass of residual oil determined.

Two procedures are specified, viz:

a) a procedure using hexane for rhombic sulfur;

b) a procedure using sulfur-saturated hexane for insoluble sulfur.

6.2 Hexane procedure

6.2.1 Reagent

6.2.1.1 Hexane, reagent grade.

6.2.2 Determination

Weigh to the nearest 1 mg, about 10 g of the sample (m_0) into a wide-mouthed 250 cm^3 conical flask and add, by pipette, exactly 100 cm^3 of hexane (6.2.1.1). Stopper and allow to stand at room temperature for 30 min, swirling the flask every 5 min. Decant 75 cm^3 of the solution thus obtained into a 100 cm^3 beaker, ensuring that no particles of sulfur are present, and pipette 50 cm^3 of this solution into another 100 cm^3 beaker. Evaporate off the solvent from this 50 cm^3 of solution by placing the beaker in a water bath in a fume cupboard. Remove the beaker from the water bath and allow to cool to room temperature. Extract the residue with 2 cm^3 of hexane, measuring the solvent from a burette and adding it in such a way that the sides of the beaker are washed down. Swirl the beaker gently to disperse the residue with the solvent. Decant the solution into a 50 cm^3 beaker previously weighed to 1 mg (m_4).

Repeat the extraction twice, collecting all the washings in the 50 cm^3 beaker. Evaporate off the solvent in a water bath and then in an oven at 80 °C for 1 h in a fume cupboard. Cool in a dessicator and then weigh immediately to 1 mg (m_5).

6.2.3 Expression of results

Calculate the oil content, expressed as a percentage by mass, using the formula

$$\frac{2(m_5 - m_4) \times 100}{m_0} - 0{,}20$$

where

m_0 is the mass, in grams, of the test portion;

m_4 is the mass, in grams, of the beaker;

m_5 is the mass, in grams, of the beaker plus oil;

0,20 is a correction to allow for the solubility of sulfur in hexane.

6.3 Sulfur-saturated hexane procedure

6.3.1 Reagent

6.3.1.1 Sulfur-saturated hexane.

Add 60 g of reagent-grade rhombic sulfur to 4 dm^3 of hexane (6.2.1.1), mix well and allow to stand for 24 h before use to allow excess sulfur to fall to the bottom of the vessel. Use only the clear supernatant liquid.

6.3.2 Determination

Weigh, to the nearest 1 mg, 5 g ± 0,01 g of the sample (m_0) into a 250 cm^3 conical flask and add 25 cm^3 of sulfur-saturated hexane (6.3.1.1). Maintain the temperature constant throughout this stage of the procedure.

Shake for 10 min and then filter through a sintered-glass filter crucible of porosity P 40 (see ISO 4793) previously weighed to 1 mg (m_6) and wash the residue with 100 cm^3 of sulfur-saturated hexane (6.3.1.1). Wash the residue twice with 25 cm^3 of reagent-grade ethyl alcohol.

Dry the filter crucible plus residue for 1 h at 80 °C in an oven in a fume cupboard, cool in a dessicator and weigh to 1 mg (m_7).

6.3.3 Expression of results

Calculate the oil content, expressed as a percentage by mass, using the formula

$$\frac{(m_0 + m_6 - m_7) \times 100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_6 is the mass, in grams, of the filter crucible;

m_7 is the mass, in grams, of the filter crucible plus residue.

6.4 Test report

The test report shall include the following particulars:

a) a reference to this International Standard and the procedure used (hexane or sulfur-saturated hexane);

b) all details necessary for the identification of the sample;

c) the oil content;

d) the date of the test;

e) details of any deviation from the standard test procedure.

7 Determination of insoluble-sulfur content

7.1 Principle

A test portion is stirred with solvent to dissolve the rhombic sulfur and any oil. The insoluble sulfur is filtered off, dried and weighed.

Two procedures are specified, viz:

a) a reference procedure using toluene as solvent;

b) an alternative procedure using carbon disulfide.

NOTE — The two procedures may give different results.

7.2 Reference procedure using toluene

7.2.1 Reagent

7.2.1.1 Toluene, reagent grade.

7.2.2 Procedure

Weigh, to the nearest 1 mg, approximately 2 g of the sample (m_0) in a 400 cm^3 beaker. Add 200 cm^3 of toluene (7.2.1.1) and a magnetic-stirrer bar. Cover with a clock glass and stir for 30 min. Filter through a sintered-glass filter crucible of porosity P 40 (see ISO 4793), previously weighed to the nearest 1 mg (m_6). Remove the toluene by suction. Wash three times with 20 cm^3 of toluene.

IMPORTANT — The sample must never be sucked completely dry before the last washing because reversion can occur due to icing of the insoluble sulfur.

Remove completely the toluene by suction, and dry the filter crucible in a drying oven in a fume cupboard for 1 h at 80 °C. Cool in a dessicator and weigh to 1 mg (m_7).

7.2.3 Expression of results

7.2.3.1 Calculate the insoluble-sulfur content, expressed as a percentage by mass of the total sample, using the formula

$$\frac{(m_7 - m_6) \times 100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_6 is the mass, in grams, of the filter crucible;

m_7 is the mass, in grams, of the filter crucible plus the residue of insoluble sulfur.

7.2.3.2 Calculate the insoluble-sulfur content, expressed as a percentage by mass of the sulfur portion of the sample, using the formula

$$\frac{\mathrm{IS_{ts}}}{\mathrm{TS_{ts}}} \times 100$$

where

$\mathrm{IS_{ts}}$ is the insoluble-sulfur content in the total sample (see 7.2.3.1);

$\mathrm{TS_{ts}}$ is the total sulfur content in the total sample (see 4.4).

7.3 Alternative procedure using carbon disulfide

7.3.1 Reagent

7.3.1.1 Carbon disulfide, reagent grade.

WARNING — Carbon disulfide is a very noxious, toxic and inflammable solvent; special safety precautions must therefore be taken, including the use of a fume hood.

7.3.2 Determination

Weigh, to the nearest 1 mg, approximately 5 g of sample (m_0) in a 250 cm^3 beaker. Add 100 cm^3 of carbon disulfide (7.3.1.1) and a magnetic-stirrer bar. Cover with a clock glass and stir for 30 min. Filter through a sintered-glass filter crucible of porosity P 40 (see ISO 4793), previously weighed to the nearest 1 mg (m_6). Remove the carbon disulfide by very light suction. Wash three times with 20 cm^3 of carbon disulfide.

IMPORTANT — The sample must never be sucked completely dry before the last washing because reversion can occur due to icing of the insoluble sulfur.

Remove completely the carbon disulfide by suction, and dry the filter crucible in a drying oven for 1 h at 80 °C. Cool in a dessicator and weigh to 1 mg (m_7).

7.3.3 Expression of results

7.3.3.1 Calculate the insoluble-sulfur content, expressed as a percentage by mass of the total sample, using the formula

$$\frac{(m_7 - m_6) \times 100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_6 is the mass, in grams, of the filter crucible;

m_7 is the mass, in grams, of the filter crucible plus the residue of insoluble sulfur.

7.3.3.2 Calculate the insoluble-sulfur content, expressed as a percentage by mass of the sulfur portion of the sample, using the formula

$$\frac{\mathrm{IS_{ts}}}{\mathrm{TS_{ts}}} \times 100$$

where

$\mathrm{IS_{ts}}$ is the insoluble-sulfur content in the total sample (see 7.3.3.1);

$\mathrm{TS_{ts}}$ is the total sulfur content in the total sample (see 4.4).

7.4 Test report

The test report shall include the following particulars:

a) a reference to this International Standard and the procedure used (toluene or carbon disulfide);

b) all details necessary for the identification of the sample;

c) the insoluble-sulfur content in the total sample and in the sulfur portion of the sample;

d) the date of the test;

e) details of any deviation from the standard test procedure.

8 Determination of thermal reversion of insoluble sulfur

8.1 General

Two methods are specified. Both have been the subject of an international cross-check and showed good repeatability and reproducibility.

Method A is an updated and improved version of the first method in ISO 8332:1993, that is solubilization of the sulfur in oil kept for 15 min at 105 °C.

Method B is a new method in which a test portion of sulfur is kept in a differential scanning calorimeter for 10 min at 105 °C and the soluble sulfur measured by high-performance liquid chromatography.

According to the international cross-check, the two methods give the same results.

8.2 Method A

8.2.1 Principle

A test portion is heated in mineral oil at 105 °C for 15 min followed by rapid cooling. The amount of insoluble sulfur remaining after this treatment is measured. Two procedures are available for this method:

a) a reference procedure using toluene as solvent when measuring the amount of insoluble sulfur;

b) an alternative procedure using carbon disulfide.

8.2.2 Apparatus

8.2.2.1 Thermostatic bath, filled with silicone oil, with magnetic stirrer, capable of being maintained at 105 °C ± 0,2 °C.

8.2.2.2 Stopwatch.

8.2.2.3 Glass test tube, 20 cm long and 42 mm in diameter, with screw cap or glass stopper.

8.2.2.4 Sintered-glass filter crucible, G-4 (or equivalent).

8.2.2.5 Thermometer, accurate to 0,2 °C between 100 °C and 110 °C.

8.2.2.6 Drying oven, maintained at 80 °C.

8.2.2.7 Magnetic stirrer.

8.2.2.8 Water bath, containing crushed ice.

8.2.2.9 Suction flask.

8.2.3 Reference procedure

8.2.3.1 Reagents

8.2.3.1.1 Toluene, reagent grade.

WARNING — Toluene is flammable and toxic.

8.2.3.1.2 White mineral oil, reagent grade.

8.2.3.2 Determination

Homogenize a representative portion (minimum 10 g) of the sample.

Pour 30 cm^3 of mineral oil (8.2.3.1.2) into a glass test tube (8.2.2.3) and add a magnetic stirrer bar.

Put the test tube into the thermostatic bath (8.2.2.1) at 105 °C ± 0,2 °C so that it is immersed to a depth of at least 10 cm and centred over the magnetic stirrer (see figure 2). 15 min after the tube has been placed in the bath, add quickly 1 000 mg ± 50 mg of sulfur, weighed to 1 mg (m_0). Immediately start the stopwatch (8.2.2.2). After 15 min ± 5 s, remove the test tube from the oil bath and immediately place it in a bath filled with water and ice (8.2.2.8) and stir for 1 min.

Add 50 cm^3 of toluene (8.2.3.1.1) and place the test tube on a magnetic stirrer (8.2.2.7) for 3 min.

Heat the sintered-glass filter crucible (8.2.2.4) for 1 h at 80 °C and cool it to ambient temperature in a desiccator. Weigh the crucible to the nearest 1 mg (m_6). Mount the crucible on a suction flask (8.2.2.9) and decant the oil-solvent-sulfur mixture through it while applying suction. Wash the sulfur five times with 20 cm^3 portions of toluene.

IMPORTANT — The sample must never be sucked completely dry before the last washing because reversion can occur due to icing of the insoluble sulfur.

After the last washing, suck the crucible as dry as possible. Dry the crucible for 1 h in the oven (8.2.2.6) at 80 °C, cool in the desiccator and weigh to 1 mg (m_7).

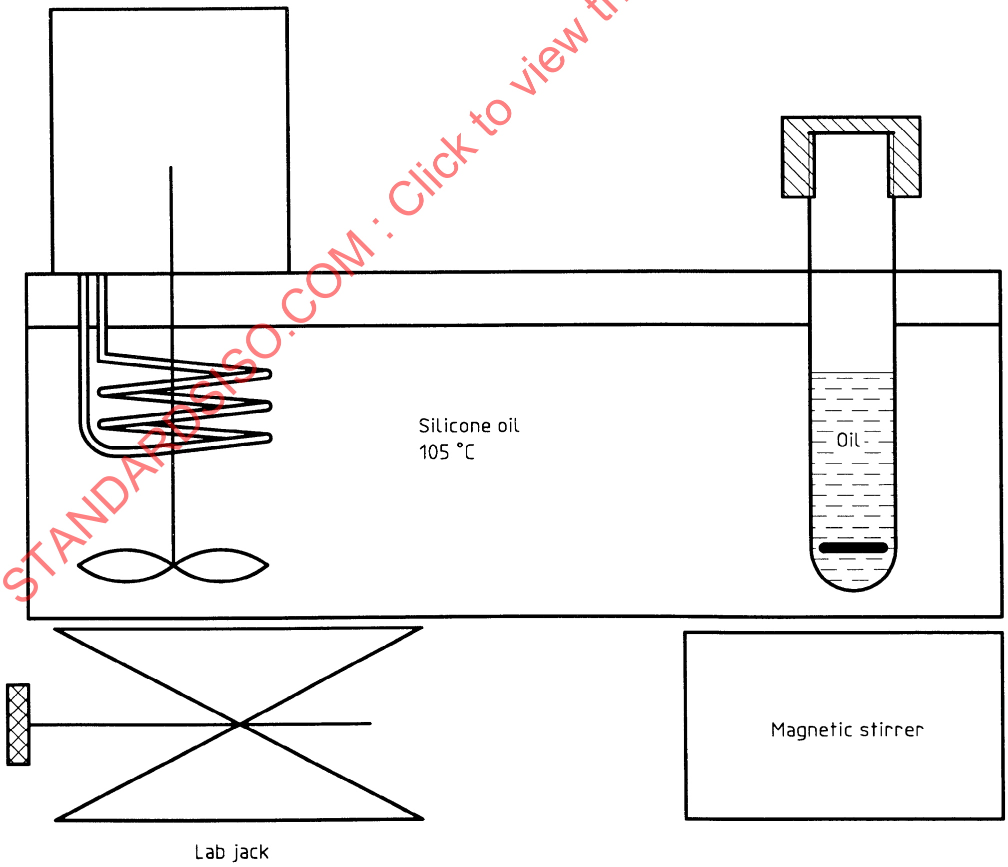

Figure 2 — Thermostatic bath with magnetic stirrer

8.2.4 Alternative procedure using carbon disulfide

8.2.4.1 Reagent

8.2.4.1.1 Carbon disulfide, reagent grade.

WARNING — Carbon disulfide is a very noxious, toxic and flammable solvent; special safety precautions must therefore be taken, including the use of a fume hood.

8.2.4.2 Determination

Homogenize a representative portion (minimum 10 g) of the sample.

Pour 30 cm^3 of mineral oil (8.2.3.1.2) into a glass test tube (8.2.2.3) and add a magnetic stirrer bar.

Put the test tube into the thermostatic bath (8.2.2.1) at 105 °C ± 0,2 °C so that it is immersed to a depth of at least 10 cm and centred over the magnetic stirrer (see figure 2). 15 min after the tube has been placed in the bath, add quickly 1 000 mg ± 50 mg of sulfur, weighed to 1 mg (m_0). Immediately start the stopwatch (8.2.2.2). After 15 min ± 5 s, remove the test tube from the oil bath and immediately place it in a bath filled with water and ice (8.2.2.8) and stir for 1 min.

Add 50 cm^3 of carbon disulfide (8.2.4.1.1) and place the test tube on a magnetic stirrer (8.2.2.7) for 3 min.

Heat the sintered-glass filter crucible (8.2.2.4) for 1 h at 80 °C and cool it to ambient temperature in a desiccator. Weigh the crucible to the nearest 1 mg (m_6). Mount the crucible on a suction flask (8.2.2.9) and decant the oil-solvent-sulfur mixture through it while applying suction. Wash the sulfur five times with 20 cm^3 portions of carbon disulfide.

IMPORTANT — The sample must never be sucked completely dry before the last washing because reversion can occur due to icing of the insoluble sulfur.

After the last washing, suck the crucible as dry as possible. Dry the crucible for 1 h in the oven (8.2.2.6) at 80 °C, cool in the desiccator and weigh to 1 mg (m_7).

8.2.5 Expression of results

Calculate the percentage thermal reversion of the insoluble sulfur using the formula

$$\left[w_S - \frac{(m_7 - m_6) \times 100}{m_0} \right] \times \frac{100}{w_S}$$

where

m_0 is the mass, in grams, of the test portion;

m_6 is the mass, in grams, of the filter crucible;

m_7 is the mass, in grams, of the filter crucible plus the residue of insoluble sulfur;

w_S is the initial insoluble-sulfur content, expressed as a percentage by mass of the total sample, calculated as in 7.2.3.1.

8.3 Method B

8.3.1 Principle

A test portion is heated at 105 °C in a differential scanning calorimeter for 10 min and the amount of soluble sulfur converted from insoluble sulfur is measured by high-performance liquid chromatography (HPLC).

8.3.2 Apparatus

8.3.2.1 Differential scanning calorimeter, calibrated in accordance with the manufacturer's specification and using indium as the temperature standard (onset).

8.3.2.2 High-performance liquid chromatograph, equipped with two pumps for programmed elution, variable-wavelength UV detector-recorder and integrator.

8.3.2.3 HPLC column, reverse-phase type.

8.3.2.4 Volumetric flasks: 1 × 100 cm^3 and 7 × 20 cm^3.

8.3.3 Reagents

8.3.3.1 Methylene chloride, reagent grade.

8.3.3.2 Rhombic sulfur.

8.3.3.3 Methanol, HPLC grade.

8.3.3.4 Water, HPLC grade.

8.3.4 Chromatographic conditions[1]

Pump A: 100 % methanol.

Pump B: 60 % methanol, 40 % water.

Flow: 80 % pump A, 20 % pump B.

Total flow: 2 cm^3/min.

Wavelength: 275 nm.

Column oven: 40 °C.

Injection volume: 50 mm^3 (20 mm^3 may be acceptable). Note, however, that it is essential to use the same injection volume both in the preparation of the calibration curve (see 8.3.5) and in the actual determination (see 8.3.7 and 8.3.8).

8.3.5 Preparation of calibration curve

Weigh 30 mg of rhombic sulfur (8.3.3.2) into a 100 cm^3 volumetric flask (see 8.3.2.4).

Add 50 cm^3 of methylene chloride (8.3.3.1). Shake till the sulfur dissolves.

Fill to the mark with methylene chloride.

Transfer 1 cm^3, 2 cm^3, 3 cm^3, 5 cm^3, 7 cm^3, 10 cm^3 and 15 cm^3 aliquots of this solution into 20 cm^3 volumetric flasks (see 8.3.2.4).

Fill each to the mark with methylene chloride.

Inject 50 mm^3 (or 20 mm^3) of each solution into the chromatograph (8.3.2.2).

Calculate the areas of the sulfur peaks.

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[1] Other conditions may be used as long as the sulfur peak is well resolved.

Plot the total amount of sulfur in each flask vs the corresponding areas.

Calculate the best-fit line either by computer or graphically.

NOTE — A calibration curve is not always necessary. Within a narrow range, two standard solutions can be assumed to define a straight-line relationship.

8.3.6 DSC programme

Starting temperature: 40 °C.

Final temperature: 105 °C.

Heating rate: 50 °C/min.

Time at 105 °C: 10 min.

Cooling rate: 50 °C/min.

If the calorimeter does not have a cooling system capable of cooling the test portion at 50 °C/min, open the sample compartment of the calorimeter immediately at the end of the heating period and transfer the contents of the pan as rapidly as possible into the 20 cm^3 volumetric flask containing 10 cm^3 of solvent.

8.3.7 Determination of initial soluble sulfur

Weigh 10 mg of the sample (m_0) into a 20 cm^3 volumetric flask.

Add to the flask 10 cm^3 of methylene chloride.

Shake the flask for 5 min.

Fill to the mark with methylene chloride.

Allow to stand for 2 h.

Inject 50 mm^3 (or 20 mm^3) of the solution into the HPLC apparatus. Use the same injection volume as was used in the preparation of the calibration curve.

Calculate the area of the sulfur peak.

From the calibration curve, determine the amount of soluble sulfur in the flask (m_8).

Calculate the soluble-sulfur content of the sample, expressed as a percentage by mass, using the formula

$$\frac{m_8 \times 100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_8 is the mass, in grams, of soluble sulfur found.

8.3.8 Determination of soluble sulfur after 10 min exposure time

Weigh 10 mg of the sample (m_0) into a DSC pan.

Without covering it, introduce it into the sample compartment of the calorimeter.

Start the DSC programme (see 8.3.6).

At the end, transfer the contents of the pan into a 20 cm3 volumetric flask containing 10 cm3 of methylene chloride.

Shake the flask for 5 min.

Fill to the mark with methylene chloride.

Allow to stand for 2 h.

Inject 50 mm3 (or 20 mm3) of the solution into the HPLC apparatus. Use the same injection volume as was used in the preparation of the calibration curve.

Calculate the area of the sulfur peak.

From the calibration curve, determine the amount of soluble sulfur in the flask (m_9).

Calculate the soluble-sulfur content of the sample after 10 min exposure time, expressed as a percentage by mass, using the formula

$$\frac{m_9 \times 100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_9 is the mass, in grams, of soluble sulfur after 10 min.

8.3.9 Expression of results

Calculate the percentage thermal reversion of the insoluble sulfur using the formula

$$(\mathrm{SS}_{10} - \mathrm{SS}_0) \times \frac{100}{(100 - \mathrm{SS}_0 - \mathrm{OIL})}$$

where

SS_0 is the initial soluble-sulfur content;

SS_{10} is the soluble-sulfur content at time 10 min;

OIL is the oil content of the sample, expressed as a percentage by mass (see clause 6).

8.4 Precision

8.4.1 General

The precision calculations to express repeatability and reproducibility were performed in accordance with ISO/TR 9272. Consult this for precision concepts and nomenclature. Annex B gives guidance on the use of repeatability and reproducibility data.

8.4.2 Interlaboratory test programme

A type 1 interlaboratory test programme was organized in 1992. Three sulfur samples, A, B and C, with different thermal reversions, were sent to the participating laboratories where they were tested using both of the test procedures.

8.4.3 Precision results

The precision results for method A are given in table 1. The precision results for method B are given in table 2.

Table 1 — Precision data for thermal reversion using method A (type 1 precision in days)

Sample	Mean level	Within lab			Between labs		
	%	s_r	r	(r)	s_R	R	(R)
A	66,75	1,03	2,86	4,28	2,28	6,32	9,47
B	66,75	0,32	0,89	1,33	2,14	5,93	8,88
C	67,49	0,26	0,72	1,07	3,36	9,31	13,79
Pooled or average values ($p = 8$, $q = 3$, $n = 2$)	67,00	0,64	1,77	2,64	2,65	7,35	10,97

s_r = Within-lab standard deviation
s_R = Between-labs standard deviation
r = Repeatability, in measurement units
(r) = Repeatability, in percent[1)]
R = Reproducibility, in measurement units
(R) = Reproducibility, in percent[1)]

1) These values represent percent relative, i.e. percent of a percent.

The repeatability r of method A has been established as 1,77 points. Two single test results (or determinations) that differ by more than 1,77 points must be considered suspect and dictate that some appropriate investigate action be taken.

The reproducibility R of method A has been established as 7,35 points. Two single test results (or determinations), obtained in separate laboratories, that differ by more than 7,35 points must be considered suspect and dictate that some appropriate investigative action be taken.

Table 2 — Thermal reversion using method B (type 1 precision in days)

Sample	Average	Within lab			Between labs		
	%	s_r	r	(r)	s_R	R	(R)
A	14,16	1,81	5,02	35,45	2,24	6,21	43,86
B	14,4	1,19	3,3	22,92	2,28	6,32	43,89
C	9,9	1,34	3,71	37,47	2,59	7,18	72,53
Pooled or average values ($p = 7$, $q = 3$, $n = 2$)	12,82	1,47	4,07	31,75	2,38	6,6	51,48

s_r = Within-lab standard deviation
s_R = Between-labs standard deviation
r = Repeatability, in measurement units
(r) = Repeatability, in percent[1)]
R = Reproducibility, in measurement units
(R) = Reproducibility, in percent[1)]

1) These values represent percent relative, i.e. percent of a percent.

The repeatability r of method B has been established as 4,07 points. Two single test results (or determinations) that differ by more than 4,07 points must be considered suspect and dictate that some appropriate investigate action be taken.

The reproducibility R of method B has been established as 6,60 points. Two single test results (or determinations), obtained in separate laboratories, that differ by more than 6,60 points must be considered suspect and dictate that some appropriate investigative action be taken.

8.5 Test report

The test report shall include the following particulars:

a) a reference to this International Standard and the method used, i.e. method A (toluene or carbon disulfide) or method B;

b) all details necessary for the identification of the sample;

c) the percentage thermal reversion of the insoluble sulfur;

d) the date of the test;

e) details of any deviation from the standard test procedure.